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6. AUTHOR(S)

Rainer A. Dressler, Skip Williams*, Susan T. Graul**,
Richard H. Salter, Edmond Murad

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Phillips Lab/WSSI
29 Randolph Road
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*Dept of Chemistry, Stanford University, Stanford CA 94305
**Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave.,
Pittsburgh, PA 15213-3890

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Rainer A. Dressler^a, Skip Williams^{a,b}, Susan T. Graul^{a,c},
Richard H. Salter^a and Edmond Murad^a

^a Phillips Laboratory, PL WSSL, Hanscom AFB, MA 01731-3010, USA

^b Department of Chemistry, Stanford University, Stanford, CA 94305, USA

^c Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213-3890, USA

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Guided-ion beam measurements of the $\text{Kr}^+ + \text{NO}$ charge-transfer reaction

Rainer A. Dressler^a, Skip Williams^{a,b}, Susan T. Graul^{a,c},
Richard H. Salter^a and Edmond Murad^a

^a Phillips Laboratory, PL WSSL, Hanscom AFB, MA 01731-3010, USA

^b Department of Chemistry, Stanford University, Stanford, CA 94305, USA

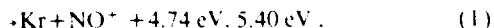
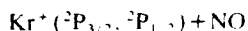
^c Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213-3890, USA

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1. Introduction

The $\text{Kr}^+ + \text{NO}$ charge-transfer reaction



is strongly exothermic, but the rate constant at thermal energies is three orders of magnitude less than the Langevin-Gioumoussis-Stevens ion-induced dipole capture rate constant [1,2]. The low efficiency of this reaction is believed to be a consequence of negligible Franck-Condon factors for the product states of Kr and NO^+ that are resonant with the reactants. This is readily seen in the photoelectron spectrum of NO^+ [3,4]. The first electronically excited state of NO^+ is the metastable $a^1\Sigma^+$ state, which lies 6.39 eV above the $X^1\Sigma^+$ ground state [5], and cannot be accessed by reaction (1) at thermal energies.

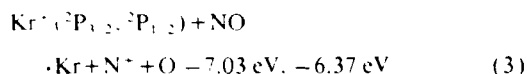
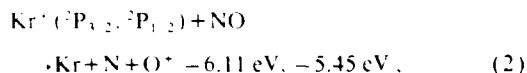
Favorable Franck-Condon factors and small energy gaps, ΔE , between reactant and product states are the most frequently cited criteria governing charge-transfer proceeding through a long-range direct mechanism at hyperthermal collision energies

[6,7]. These criteria arise from nonadiabatic transition theory in molecular collisions [8,9]. Although suggesting that the low rate was due to energy resonance and Franck-Condon constraints, the thermal energy ICR experiments of Laudenslager et al. [1] could not determine whether the importance of Franck-Condon overlap was due to a predominance of a direct process in the thermal charge-transfer reactions, or whether Franck-Condon arguments also apply to mechanisms involving longer-lived collision complexes.

Recently, we have studied the energy dependence of the $\text{Ar}^+ + \text{NO}$ and $\text{N}_2^+ + \text{NO}$ collision systems in a guided-ion beam experiment [10]. The collision energy dependence of the charge-transfer cross section as well as charge-transfer product ion time-of-flight (TOF) measurements indicated that both direct charge transfer and the formation of long-lived intermediates play important roles at hyperthermal energies. The relatively large cross sections observed were attributed to resonance with excited electronic states of the products that exhibit significant Franck-Condon overlap with the reactant states. Efficient translational energy transfer was observed to occur in those charge-transfer collisions in which a long-

lived intermediate complex was formed. Interestingly, excited product states with substantial Franck-Condon overlap appear to be preferentially populated in those collisions. These results, as well as the low thermal rate of charge-transfer reaction (1), imply that Franck-Condon criteria similar to those governing nonadiabatic transitions in molecular collisions are also of importance when longer-lived intermediates are involved.

In this Letter, we present guided-ion beam measurements of the $\text{Kr}^+ + \text{NO}$ charge-transfer cross section at collision energies ranging from thermal to 16 eV. The only known previous measurement of hyperthermal $\text{Kr}^+ + \text{NO}$ charge-transfer cross sections is that of Kobayashi [11], who determined cross sections up to a collision energy of ≈ 2 eV in a static drift tube. The present results agree with the drift-tube measurements at collision energies below 1 eV but differ at higher energies. Measurements of the cross sections for the dissociative charge-transfer reactions



are also presented. The energy dependence of the charge-transfer cross section exhibits interesting features that further clarify the role of energy resonance and Franck-Condon overlap in ion-molecule charge-transfer systems.

2. Experimental

The guided-ion beam apparatus has been previously described in detail [12] and will only be discussed briefly here. Krypton ions are produced in an electron impact ion source at electron energies of ≈ 20 eV. It is assumed that the primary ion beam consists of a statistical ratio of spin-orbit states. The ions are passed through a Wien velocity filter for mass selection. The transmission energy in the velocity filter is only 120 eV, and the mass resolution therefore does not suffice to select a single Kr isotope. The low

transmission energy is chosen to minimize the formation of fast metastable Kr atoms, which are produced through ion-surface charge-neutralization collisions with the Wien filter electrode surfaces. These metastables can enter the collision region and form NO^+ through Penning ionization collisions with NO.

Following passage through the Wien filter, the ion beam is decelerated and injected into a system of two rf octopoles in series. The ion energy within the injection electrode is less than 500 meV to prevent rf heating in the injection stage. This in turn preserves the ion translational energy distribution which has a half-width of 300 meV. A 10 MHz rf voltage is applied to the octopoles to create a cylindrical ion trapping potential within which the ion-molecule collisions occur. The first octopole passes through a 3.5 cm long collision cell containing the NO gas. The NO density is measured with a capacitance manometer and is ≈ 0.250 mTorr. The product ions formed are guided into the second octopole. Backscattered product ions are reflected into the forward direction by a small potential barrier induced by a cylindrical electrode surrounding the octopole at the collision chamber entrance. The second octopole is biased ≈ 0.4 V lower than the first in order to give slow ions sufficient kinetic energy to overcome barriers due to surface potential inhomogeneities. The collection efficiency of product ions is nearly 100%.

Product and primary ions are extracted from the second octopole and focused into a quadrupole mass analyzer. The ions are detected with a channel plate that is situated off axis. The energy dependence of the cross section is determined by scanning the octopole bias potential, and thus the ion energy, while monitoring product ion and reactant ion count rates. The cross section for forming product ions is calculated from

$$\sigma = \frac{I_{\text{prod}}}{(I_{\text{reac}} + I_{\text{prod}})nl}, \quad (4)$$

where I_{reac} is the primary ion intensity, I_{prod} is the product ion intensity, n is the target gas density and l is the effective interaction length which is calibrated based on measurements using a known reaction system. Due to the significant metastable content in the beam, a fraction of the charge-transfer

product ions is attributable to Penning ionization. This fraction is determined by measuring the NO^+ signal when the ion beam is deflected off the instrument axis using a split-pair electrode in the injection lens.

3. Results and discussion

The energy dependence of the charge-transfer cross section is shown on a logarithmic scale in fig. 1. The guided-ion beam data are compared to drift-tube measurements of Kobayashi [11]. At collision energies below 1 eV, the present results are in excellent agreement with the drift-tube data. At these energies, the cross section decreases exponentially with collision energy, yielding an $E_T^{-0.4}$ power fit. Whereas the cross sections measured in the drift tube begin to increase with collision energy at ≈ 0.8 eV, the guided-ion beam cross sections are only observed to increase at collision energies above 3 eV. At collision energies above 8 eV, the cross section drops again with collision energy.

The discrepancy between the energy dependence of the drift tube and the guided-ion beam cross sections may be related to the different collision energy distributions in the two experiments. In drift-tube experiments, the nominal collision energy is derived from the Wannier formula [13]. At high electric field

strengths the relative velocity distribution is substantially broadened through the random motion of the ions resulting in an energy width that is proportional to E_T . The nominal energy in the guided-ion beam work is the maximum of a thermally broadened, Gaussian collision energy distribution and is proportional to $E_T^{-1/2}$ [14]. As a consequence, the relative translational energy distribution at hyperthermal energies is significantly broader than that encountered in the guided-ion beam experiment [15]. The fact that the cross-section minimum occurs at lower collision energies in the drift-tube experiment than in the guided-ion beam experiment is consistent with the difference in experimental collision energy distributions.

The differences in the observed cross sections at higher collision energies could also be attributed to different Kr^+ spin-orbit state populations encountered in the two experiments. As mentioned in section 2, we assume a statistical ratio of 2:1 between the $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ states of Kr^+ . In the drift-tube experiment, it may be assumed that most of the primary ions are in the ground spin-orbit state. Significant differences in the spin-orbit state reactivities could thus lead to noticeably different observed cross sections. As will be shown later in this Letter, our interpretation of the energy dependence of the charge-transfer cross section is inconsistent with this argument.

In fig. 2, the energy dependence of the dissociative charge-transfer cross sections (reactions (2) and (3)) is compared with the charge-transfer cross sections on a linear scale. The arrows indicate the respective thresholds assuming ground-state reactants and are in very good agreement with the N^+ and O^+ onsets (eqs. (2) and (3)). Despite the assumption that $\approx 30\%$ of the primary ion beam consists of Kr^+ ($^2\text{P}_{1/2}$) ions, no N^+ and O^+ could be detected at the respective Kr^+ ($^2\text{P}_{1/2}$) + NO thresholds, which lie 0.66 eV below those of Kr^+ ($^2\text{P}_{3/2}$) + NO reactants. This is an indication that excited spin-orbit reactants play a minor role in forming products with internal energy that exceed the N^+ and O^+ thresholds.

The $E_T^{-0.4}$ dependence observed at low energies indicates that complex formation plays a key role in forming charge-transfer products at these energies. The low-energy cross sections are, however, approximately two orders of magnitude smaller than the

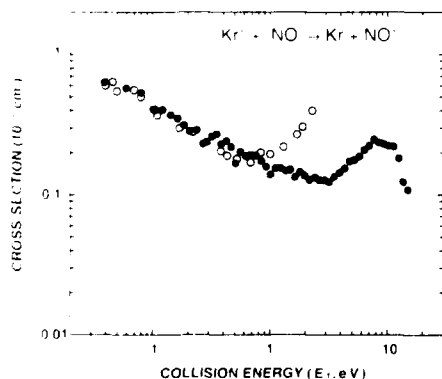


Fig. 1. Energy dependence of the $\text{Kr}^+ + \text{NO}$ charge-transfer cross section. The guided-ion beam data are compared to drift tube measurements of Kobayashi [11]. (●) This work. (○) Kobayashi (drift tube).

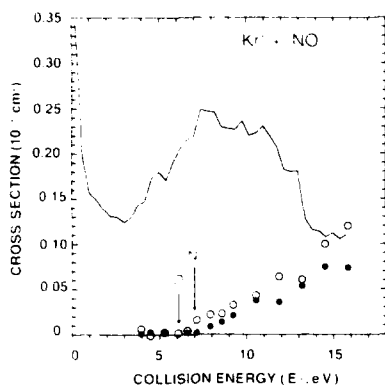


Fig. 2. Energy dependence of dissociative charge-transfer reactions (2) and (3). The charge-transfer cross section is shown for comparison. The arrows indicate the respective thermodynamic thresholds: (●) N^+ , (○) O^+ , (□) NO^+ .

LGS capture cross section for an ion-induced dipole interaction. The observed cross sections are also considerably smaller than the cross sections for complex-forming charge-transfer collisions determined from time-of-flight measurements in the $Ar^+ + NO$ and $N_2^+ + NO$ systems [10]. In the former of those systems, for example, a cross section for charge-transfer through complex formation of $(1.2 \pm 0.4) \times 10^{-16} \text{ cm}^2$ is derived at a collision energy of 2.16 eV, whereas the integral charge-transfer cross section in the $Kr^+ + NO$ charge-transfer system is only $0.13 \pm 0.05 \times 10^{-16} \text{ cm}^2$. Because the energy dependence and magnitude of the LGS cross sections only depend on the polarizability of the target molecule, the complex formation rates are similar for the various reactant ions. This suggests that only a small fraction of the long-lived $(KrNO)^+$ collision complexes decay to charge-transfer products at low energies.

At the highest collision energies studied, the cross sections for dissociative charge transfer are comparable to those of charge transfer. The increase with energy of the dissociative charge-transfer cross sections coincides with a decrease of the charge-transfer cross section, indicating that the decrease is due to a loss of charge-transfer products due to dissociation. The marked effect on the charge-transfer cross section implies that translational energy is efficiently transferred into internal modes in $Kr^+ + NO$ charge-

transfer collisions, leading to a large fraction of products with internal energies far exceeding that available from the exothermicity of the reaction. Such efficient energy transfer may either occur in very small impact-parameter collisions, or through the formation of long-lived intermediate complexes allowing for a redistribution of energy. In the recent experiments conducted in this laboratory on the $Ar^+ + NO$ and $N_2^+ + NO$ charge-transfer systems [10], time-of-flight measurements showed that products formed in the decay of a collision complex with lifetime exceeding several rotational periods exhibit high internal excitation. In those systems, the observed product internal energies correspond almost exclusively to energy levels with significant Franck-Condon factors, suggesting that a requirement for Franck-Condon overlap imposes restrictions on the statistical redistribution of energy within the intermediate long-lived complexes.

The energy levels of the $Kr^+ + NO$ charge-transfer system are shown in fig. 3. Those vibrational levels are shown that exhibit significant intensities in the NO photoelectron spectrum [3,4] and thus have substantial ionization Franck-Condon factors. It is seen that the reactants are resonant with an energy region where the Franck-Condon overlap is negligible. Energy resonance and Franck-Condon models [6,7] thus predict a very small direct charge-transfer cross section, which is clearly confirmed by the pres-

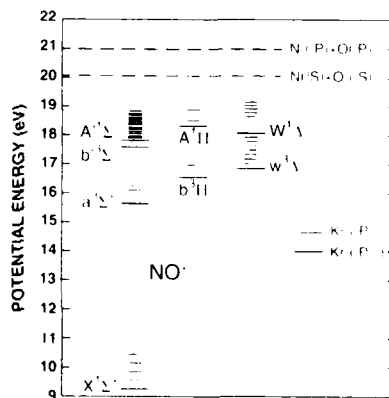


Fig. 3. Energy level diagram of the $(Kr+NO)^+$ charge-transfer system. Those vibrational levels are indicated that have significant Franck-Condon overlap.

ent results. The $\text{Kr}^+ + \text{NO}$ charge-transfer cross sections at hyperthermal energies are almost two orders of magnitude smaller than those observed for the $\text{Ar}^+ + \text{NO}$ and $\text{N}_2^+ + \text{NO}$ charge-transfer systems [10].

The increase observed in the charge-transfer cross section at energies exceeding 3 eV may be a consequence of the fact that several excited electronic product states of NO^+ become energetically accessible. In addition, the low vibrational levels of these excited states have significant Franck-Condon factors. The minimum collision energy required to access the first electronically excited state is 1.7 eV for ground-state $\text{Kr}^+ + \text{NO}$ reactants. The fact that a large fraction of charge-transfer products are formed in states close to and above the dissociation limits of NO^+ is evidenced by the efficient dissociative charge-transfer channel. The picture that thus emerges, is that due to the sudden increase at higher collision energies of the number of accessible states with significant Franck-Condon overlap, the fraction of long-lived complexes that decay to charge-transfer products increases dramatically.

This interpretation implies that the charge-transfer cross section minimum of the $\text{Kr}^+ (^2\text{P}_{1/2}) + \text{NO}$ charge-transfer reaction should be observed at lower energies than that of ground-state reactants. The cross section minimum observed in this work is, however, at higher collision energies than that observed in a drift-tube experiment, where fully relaxed reactants may be expected [11]. We, therefore, believe that the differences between the drift-tube work and the present results are not related to effects due to the excited spin-orbit state of Kr^+ , but are most likely attributable to different collision energy distributions.

Comparison of the small charge-transfer cross sections observed for this non-resonant system with the significantly larger cross sections measured for the near-resonant $\text{Ar}^+ + \text{NO}$ and $\text{N}_2^+ + \text{NO}$ reactions [10], and consideration of the highly unfavorable Franck-Condon factors for direct charge transfer in reaction (1), implies that charge transfer in the $\text{Kr}^+ + \text{NO}$ reaction proceeds largely via intimate collisions, involving either long-lived complex formation or small impact parameters.

4. Conclusions

The charge-transfer reaction of Kr^+ and NO is very inefficient through the collision energy range of 0.08 eV to 16 eV. The reaction proceeds mainly via complex formation or small-impact parameter impulsive collisions. Formation of the dissociative charge-transfer products N^+ and O^+ is observed at their thermochemical thresholds, and competes efficiently with non-dissociative charge transfer above about 8 eV, suggesting that energy transfer is efficient within the intimate collisions. Direct charge transfer via large-impact parameter collisions is probably not a significant mechanism in this system.

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